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To: Dr. D. Mills
Director of Research

PREPARATION OF HIGH TEMPERATURE SUPERCONDUCTORS

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Potential applications of superconductors in the Ontario Hydro system appear more realistic with the discovery of high temperature superconductors (HTSC). Since the new HTSC are more complex than the metallic superconductors, and because their properties and therefore their performance depends on processing parameters, it is important to develop Ontario Hydro's capabilities in the various aspects of HTSC material technology. This will facilitate the identification and evaluation of materials and devices which will be of potential benefit to the corporation. This report summarizes the results of the work undertaken by the Utilization Section in the materials area of HTSC. Ceramic superconductors based on the yttrium-barium-copper oxide system were prepared consistently. Some of the properties of these materials were determined, analysed and compared to results reported in the literature. Recommendations for future work in the materials area of HTSC are suggested.

INTRODUCTION

Since the report of its discovery was issued in March 1987 /1/, high temperature superconductors (HTSC) have ignited an unprecedented interest in the scientific and engineering communities. This is due to the significant potential impact of this class of new materials on many future technological advances as well as on numerous present day applications. Recognizing the importance of the develpments in this area and the potential impact on its operational systems, Ontario Hydro formed a HTSC Task Force to monitor the advances in this area, to assess its potential impact on the Ontario Hydro systems and to identify short and long term applications and research opportunities related to the new HTSC materials /2/.

An Interim Task Force Report On High Temperature Superconductivity /3/ issued January, 1988, recommended a strategy for Ontario Hydro calling for "close monitoring of research trends, feasibility assessment and ranking of potential applications". It also recommended that the "Corporation undertake a 2-year work program with major tasks in information gathering, application studies, and material technology".

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As part of the materials technology program, HTSC ceramics were prepared in order to have a 'hands on' experience, and to develop the capabilities that will be essential if any future activities are to be undertaken in the area of HTSC applications, utilization, assessments and/or characterization. Materials prepared by the Utilization Section of OHRD were displayed on several occasions including: the Open House commemorating the 75th Anniversary of OHRD, held in June 1987; the visit by A.F. Baljet to EPRI in August 1987; and, the visit of Ontario Ministry of Energy staff to OHRD in September 1987. Also a paper /4/, based on measurements undertaken on samples prepared by the Utilization Section, was presented by Dr. P. Mayer (Metallurgy Department) at the "High T_c Superconductivity Workshop" held at the University of Western Ontario, September 11, 1987.

This report summarizes the processing of various compositions of high temperature superconductors and some of their properties. Recommendations for future research activities are also suggested.

MATERIALS PREPARATION

The basic HTSC compound is formed from the oxides of yttrium (Y), barium (Ba) and copper (Cu) and has the composition $YBa_2Cu_3O_7$; because of its formulation it is commonly referred to as the '1-2-3' material. To prepare this compound, the correct molar percentages of high purity powders of yttrium oxide (Y_2O_3), barium carbonate ($BaCO_3$) and copper oxide (CuO) were thoroughly mixed. The mixture was placed in a high temperature container and heated, in air, to a temperature of 930°C. Dwell time at this temperature was about 15 hours. A quick weight loss measurement indicated that the material had lost most of the carbon dioxide (CO_2) initially present in $BaCO_3$. This process is known as "calcination". The calcined material was ground, pressed into 1.2 cm diameter disks and fired at 980°C. After a dwell period of about 10 hours at this temperature, the kiln temperature was allowed to cool naturally to room temperature. The ceramics formed exhibited the Meissner effect (ie. the expulsion of magnetic field from the bulk of the sample) at liquid nitrogen temperature (77°K) which is indicative of the superconducting nature of the material. Figure 1 shows the Meissner effect for a sample prepared in our laboratory.

A second HTSC compound was also prepared using the above recipe. In this compound yttrium was replaced by another rare earth element: samarium (Sm), keeping the molar composition unchanged ie. the 1-2-3 compound. In this case it was determined that the calcination and sintering temperatures of this compound were about 50°C lower than that with yttrium. Again, these ceramics exhibited the Meissner effect at 77°K.

In the search for superconductors with higher transition temperatures, compounds with a 1-2-3 composition containing flourine (F) (partially replacing the oxygen atoms) and cerium (Ce) (partially replacing the Y atoms) were also prepared from their respective raw materials in a similar manner as described above. The following section summarizes the superconducting properties of the various 1-2-3 compounds prepared.

PROPERTIES

1. Crystal Structure

X-ray diffraction (XRD) profile of the calcined 1-2-3 powder (Figure 2) indicated that the compound is predominantly the superconducting orthorhombic phase with less than 2% of secondary phases present. The lattice parameters, of the orthorhombic phase as determined from the (200), (020) and (006) diffraction peaks of Figures 2, 3 and 4 are: a=3.818 A°, b=3.894 A° and c=11.682 A° respectively. These results are in excellent agreement with results

reported in the literature/5,6/. The same result was obtained for the 'as sintered' ceramics as shown in Figure 3. When a thin surface layer (0.25 mm) was shaved off the surface, the XRD pattern of the bulk material indicated that the total amount of impurity phases present in this case is less than 0.5% of the predominant orthorhombic phase (Figure 4). The diffraction peaks between the 2Θ value of 27° and 32° are characteristic of the 'green' Y_2BaCuO_5 phase which was first thought to be the HTSC phase/7/. Also a comparison of the XRD profiles of Figures 2, 3 and 4, indicate that the relative diffraction peak intensities are similar for the powder and 'as sintered' forms but differ from that of the bulk material. The latter is in excellent agreement with calculated intensity values/5/ for the 1-2-3 orthorhombic (superconducting) phase. The observed variations in peak intensities are attributed to the preferred orientation of the (003), (005) and (006) crystallographic planes, ie. the **ab** crystallographic planes align along the surface of the ceramic. This alignment is a result of mechanical grinding in the case of the powders and mechanical pressing in the case of the ceramic disc. Fortunately, optimum transport properties in the plane of the film is achieved with this crystallographic orientation/8/.

2. Microstructure

Scanning Electron Microscope (SEM) was used to have a closer look at the grains of the ceramics prepared. The surface topography of an 'as sintered' sample, shown in Figure 5, indicates that grains are closely packed with very few voids. The average grain size is about 11 micrometers; in ceramic terms this is relatively large and indicates excessive heating during sintering. It also appears that some impurities in the form of smaller particles are present in the ceramic. The topography of a fracture surface of the same sample is shown in Figure 6. Grains in this case are not as closely packed as those on the surface. This is a result of uneven load application during powder pressing and/or non-uniform heating during sintering. Grains having a plate-like structure are also evident in Figure 6. The large face of these grains is parallel to the surface of the disc sample suggesting crystallographic alignment as described in the previous section. In addition, twinning (ie. crystals aligning next to each other at 90° or 180° to relieve the stress caused by a phase transformation) manifested by parallel fine lines within a grain, also appear to exist in some grains. Figure 7 shows a clear example of twinning in a single grain. Also clearly evident in Figure 7 (and to a lesser degree in Figure 6) is the presence of fine structures on the surface of the grains. Twinning was more pronounced in a 1-2-3 sample heated near its melting point of 1000°C. As shown in Figure 8 twinning in this case was observable, using an optical microscope, at the low magnification of 100.

Energy Dispersive X-ray (EDX) analysis undertaken on the same sample examined by SEM showed that the surface of the 'as sintered' ceramic contained yttrium, barium and copper with atomic ratios of 1.5:2.1:3 respectively. This indicates an excess of yttrium on the surface of the ceramic suggesting that excessive heating occurred during the sintering process (confirming the same conclusion from the grain size measurements) which resulted in the evaporation of some of the copper and barium elements; as a result, the green, yttrium-rich Y_2BaCuO_5 compound was formed on the surface of the ceramic. As mentioned in the previous section, the presence of this phase was confirmed by x-ray diffraction tests. For the fractured surface, on the other hand, EDX examination showed a 1.2:2:3 ratio; considering experimental errors and statistical deviations of this technique, this composition is in very good agreement with the 1:2:3 compound.

3. Transition Temperature

The transition temperature of several samples was measured by Dr. F. Chu and Mr. R. Cilic (Stations and Underground Section, Electrical Research Department). A four-terminal technique was used in which a constant current passes through the sample via two terminals while the

voltage drop across the sample is measured using the other two leads. The temperature of the sample was measured by a thermocouple in contact with it. Figures 9 and 10 show the transition curves for an ordinary 1-2-3 material and a flourinated 1-2-3 compound (initial composition $YBa_2Cu_3O_5F_2$). Clearly the flourinated 1-2-3 sample has a lower T_c than the regular (completely oxidized) 1-2-3 sample. This is in contradiction with an earlier report /9/ of T_c=155°K for a flourinated 1-2-3 compound with the same composition. Subsequent reports /10/ confirmed that flourinated samples have transition temperatures not higher than 93.4°K.

On the other hand, ceramics prepared by partially substituting (10 and 25%) Y by Ce did not exhibit the Meissner effect at liquid nitrogen temperature. Cerium, praseodynium (Pr) and terbium (Tb) are the only lanthenide elements (elements with an atomic number between 58 and 71) that have a stable oxidation state of 4 (the other elements, including Y have a valence of 3). It was reported /11/ that the complete replacement of Y with any of the lanthenides (except Ce,Pr and Tb) will result in a HTSC with a critical transition temperature near 90°K. These results indicate that, among other relevant parameters, the valency of the element substituting Y plays an important role in the superconducting behaviour of the 1-2-3 material.

4. Other Properties

Laser Raman spectrum, at room temperature, of a $SmBa_2Cu_3O_7$ prepared by the Utilization Section, was determined by Dr. L. Mannik (Science Section, Electrical Research Department) /12/. The frequencies of the observed Raman shifts at 425, 515, 580 and 639 cm^{-1} are similar to those observed /13,14/ for $EuBa_2Cu_3O_7$ samples. Such information is useful for phase identification and providing information on lattice vibrations which could help understand the mechanism(s) for HTSC. Raman spectrum for 1-2-3 samples based on the yttrium element could not be detected. Other investigators /12/ were also unsuccessful in determining the complete spectra for this compound; only a very weak band centered at 505 cm^{-1} was observed.

The density of the various samples prepared was determined using Archemides' displacement principle. Density values varied between 4.3 g/cm^3 and 5.54 g/cm^3 corresponding to 68% and 87% of the theoretical density value of 6.35 g/cm^3 which is derived from x-ray lattice parameter data and the atomic weights of the HTSC elements. Highest densities were obtained when a sintering temperature of 990°C was used.

In addition to preparing solid ceramic samples in the form of discs or pellets, we were able to fabricate HTSC in the form of wires, flexible tapes and ceramic rings. Such forms and shapes are of practical use and are essential if ceramic superconductors are to be used in any of the Ontario Hydro systems. For example, wires are required for transport applications while rings could be used for storage applications. Figure 11 shows the various forms of HTSC prepared at the Utilization Section laboratory.

RECOMMENDATIONS

Based on the most recent developments in the area of HTSC materials and on the results of this study, the following programs on the material processing aspect of HTSC are suggested:

1. Prepare new HTSC materials based on the bismuth-strontium-calcium-copper oxides. These HTSC have a critical transition temperature near 110°K, ie. 20°K higher than the Y-Ba-Cu oxide material.

2. Optimize fabrication procedure for HTSC by undertaking a systematic study to determine the effect of processing parameters (eg. sintering temperature and duration, rate of temperature increase and control of particle size) on the important properties (eg. critical

current and magnetic field) of the different classes of HTSC. The knowledge of sample history and the relevant characteristics of the material under test are essential if any useful in-house characterization facilities and expertise are to be developed.

3. Develop novel processing techniques utilizing microwave energy. It is expected that processing time will be considerably reduced to 3-5 hours from the 20 hours duration presently required with conventional techniques. Also, attempts will be made to form fibrous HTSC single crystal grains using microwaves. Materials having this microstructure were reported /15/ to have a critical current value two orders of magnitude larger than the polycrystalline powder ceramics. Our previous experience with microwave processing of ceramics /16/ indicates that ceramic single crystal fibres could be produced when optimum microwave parameters are used in the calcination process.

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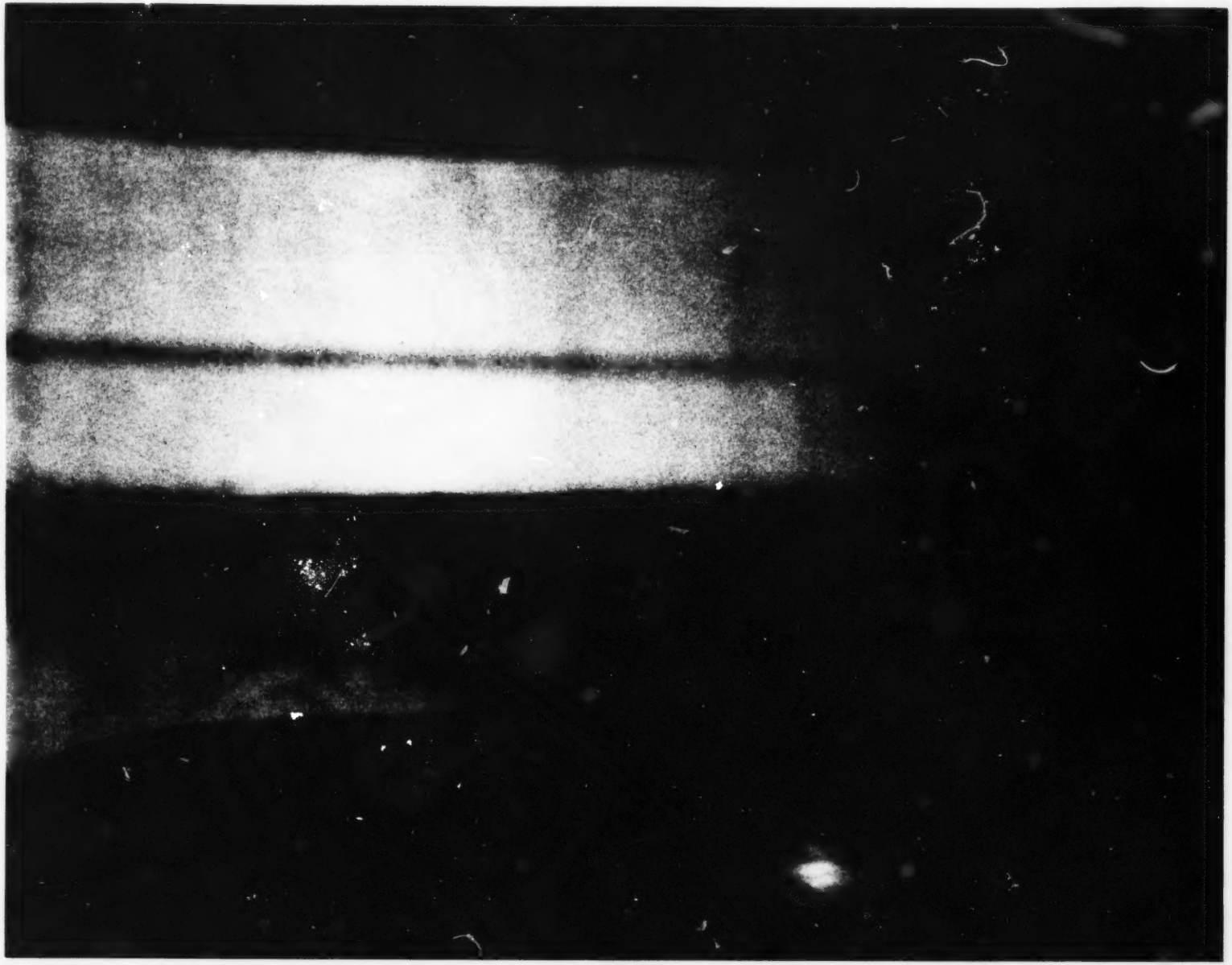

FIGURE 1

MAGNETIC LEVITATION USING HTSC PREPARED IN THE PROCESS APPLICATIONS LABORATORY

FIGURE 2

XRD OF CALCINED HTSC

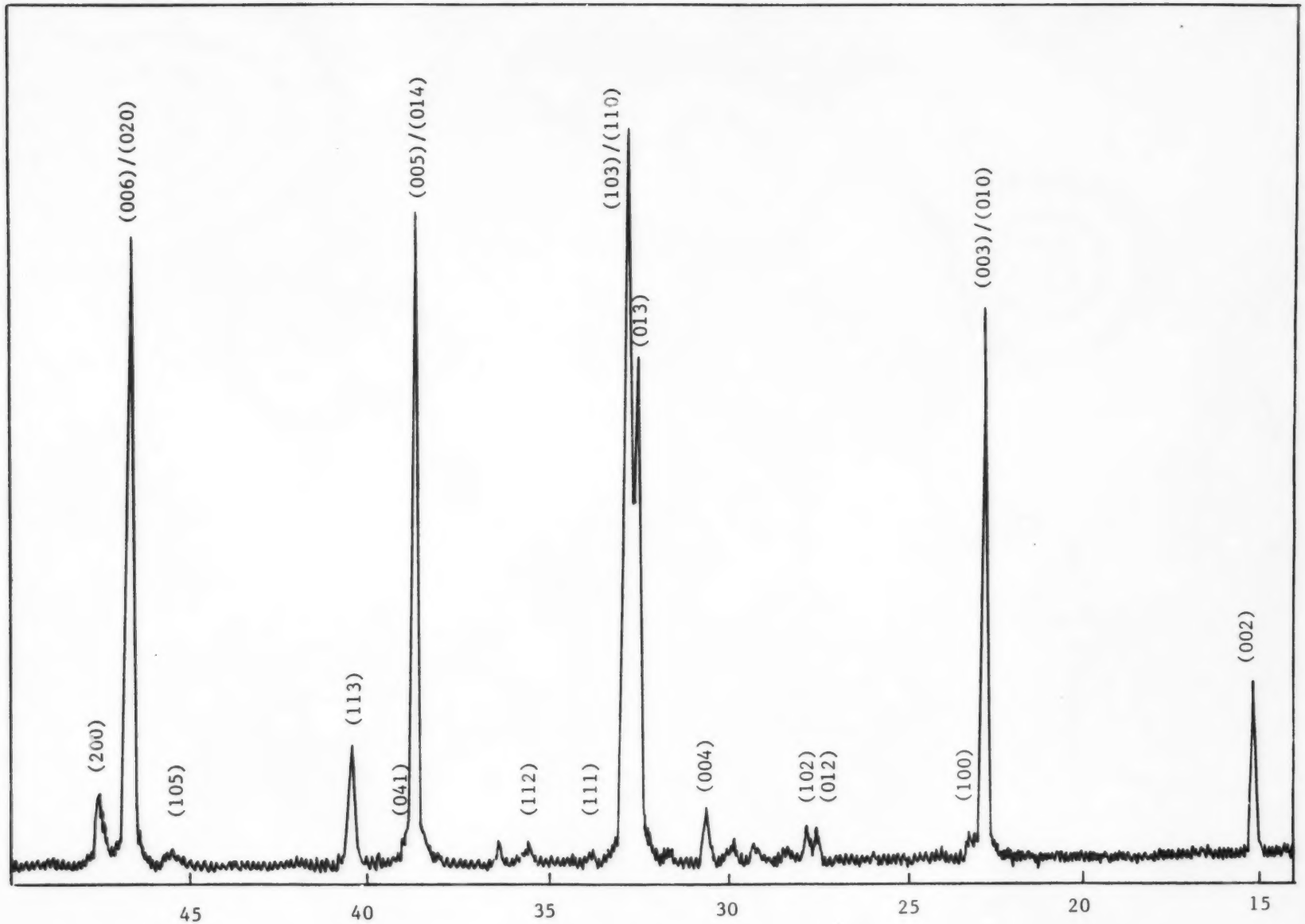

FIGURE 3

XRD OF AS SINTERED HTSC CERAMIC

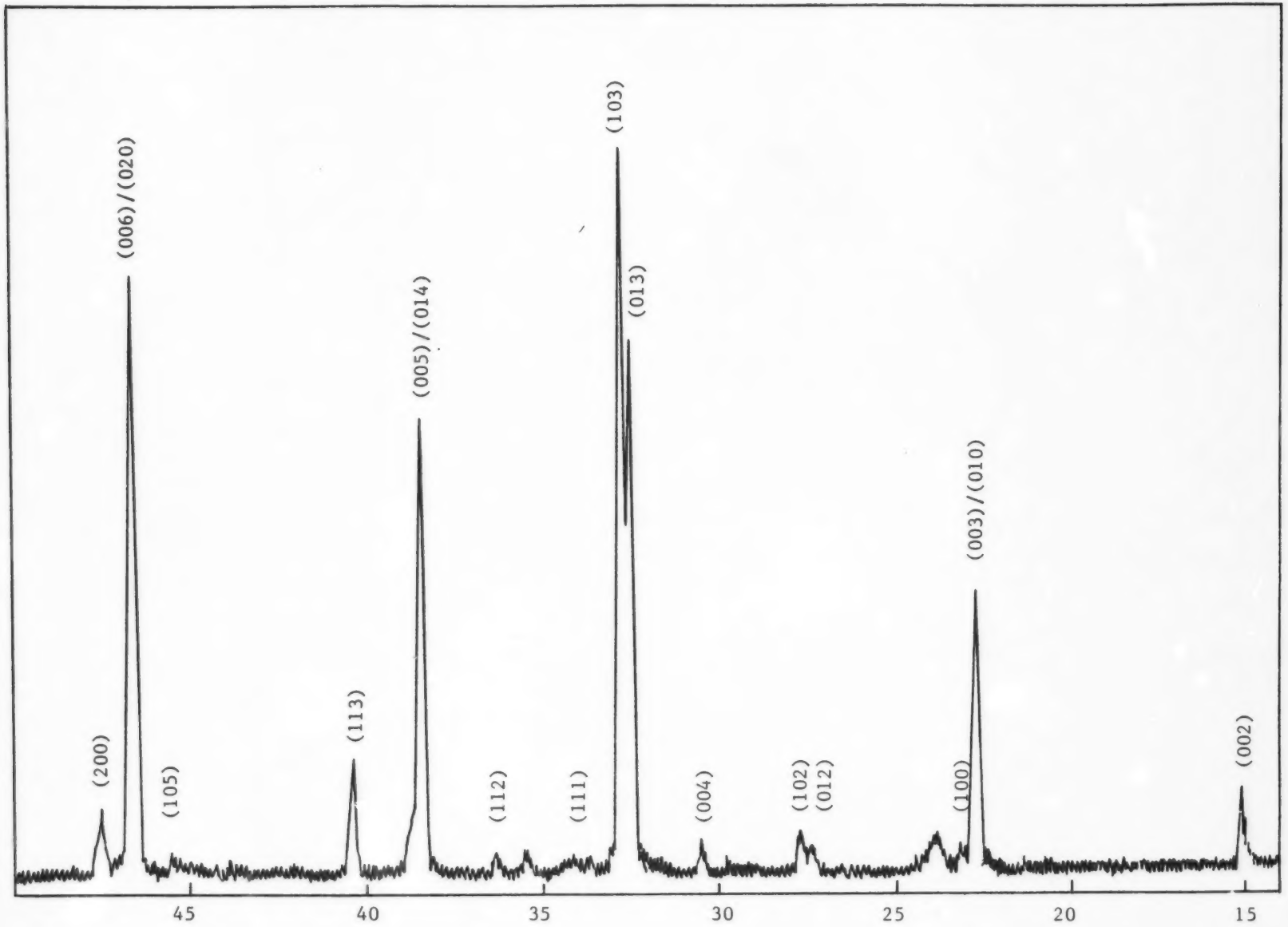

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FIGURE 4

XRD OF SHAVED SURFACE OF HTSC CERAMIC

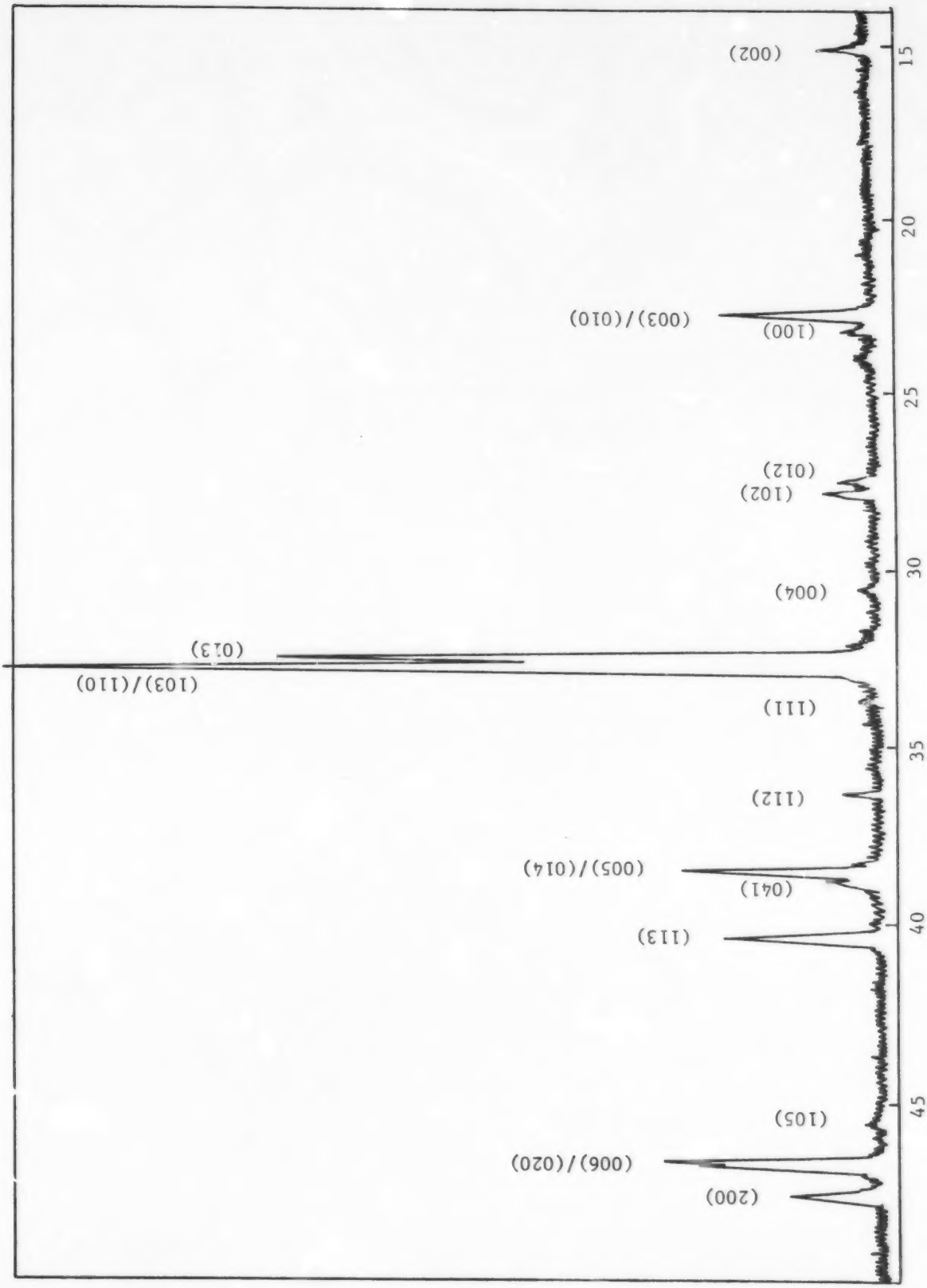

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FIGURE 5

SEM OF AS SINTERED CERAMIC SURFACE

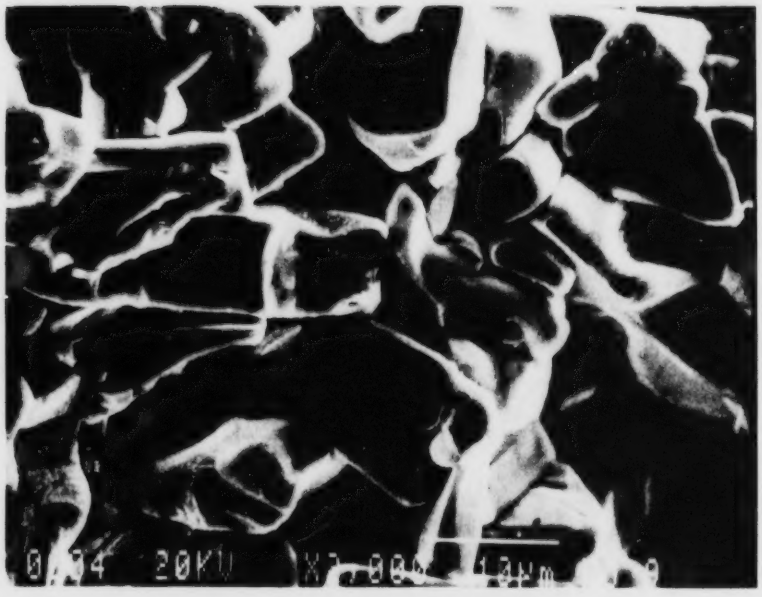

FIGURE 6

SEM OF FRACTURED SURFACE OF SINTERED CERAMIC

FIGURE 7

TWINNING AND GRAIN BOUNDARY LAYER IN HTSC

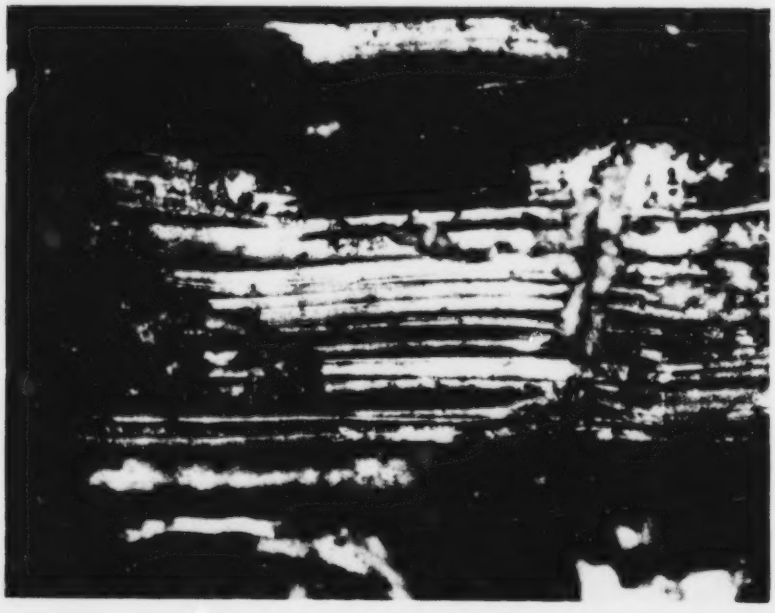

FIGURE 8

TWINNING IN HTSC SINTERED NEAR ITS MELTING POINT

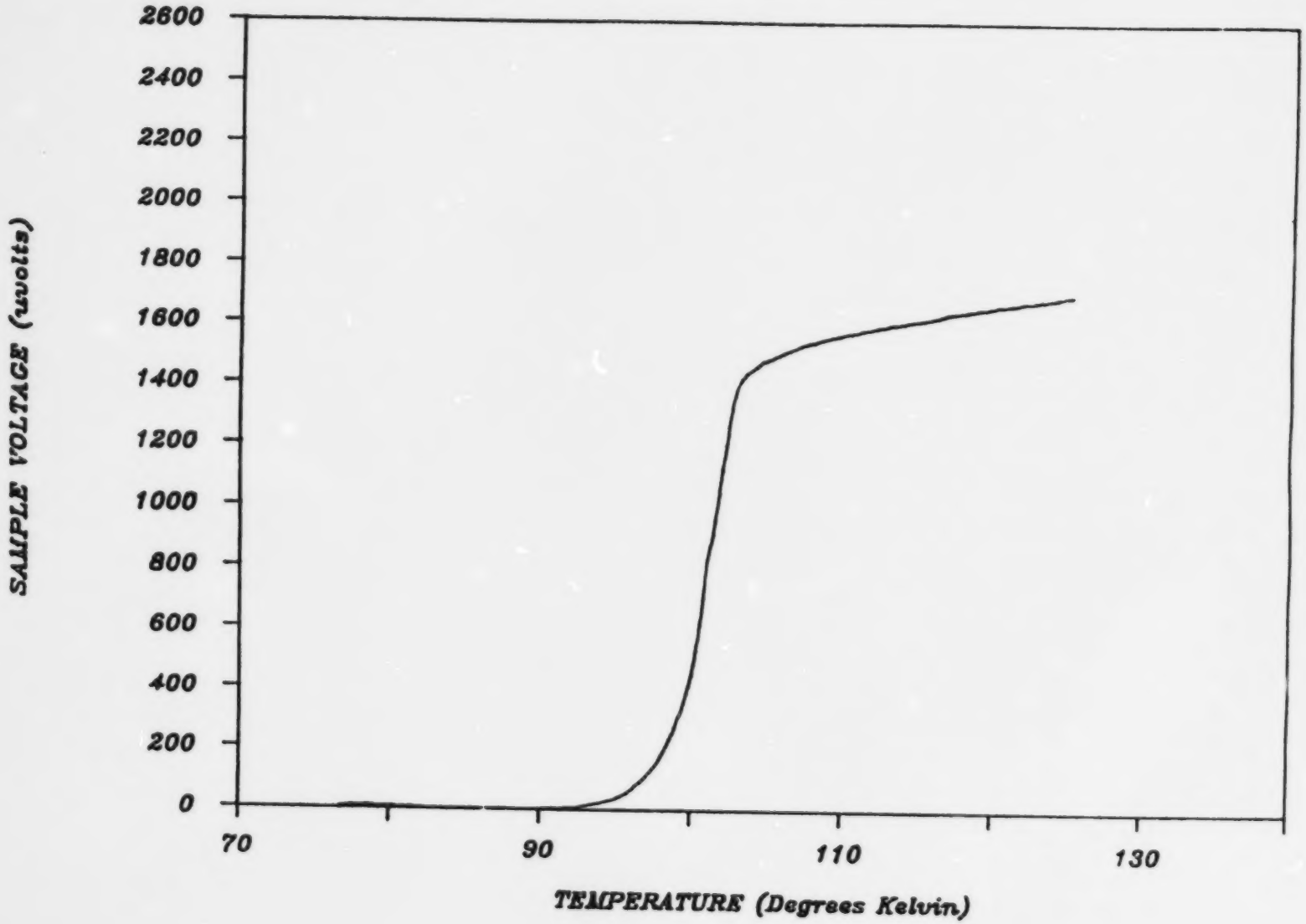

FIGURE 9

TRANSITION CURVE FOR 1-2-3 HTSC

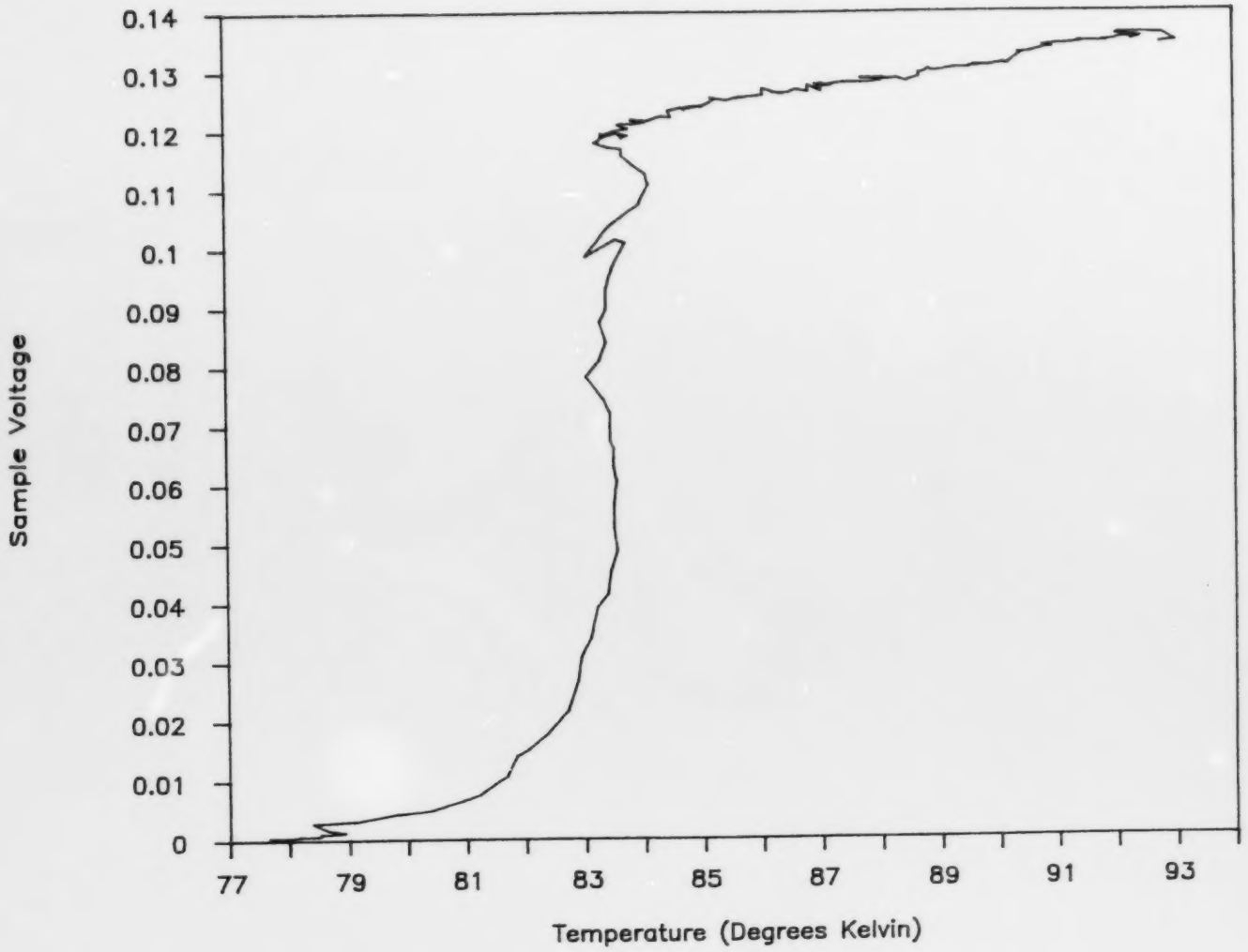

FIGURE 10

TRANSITION CURVE FOR FLOURINATED 1-2-3 HTSC

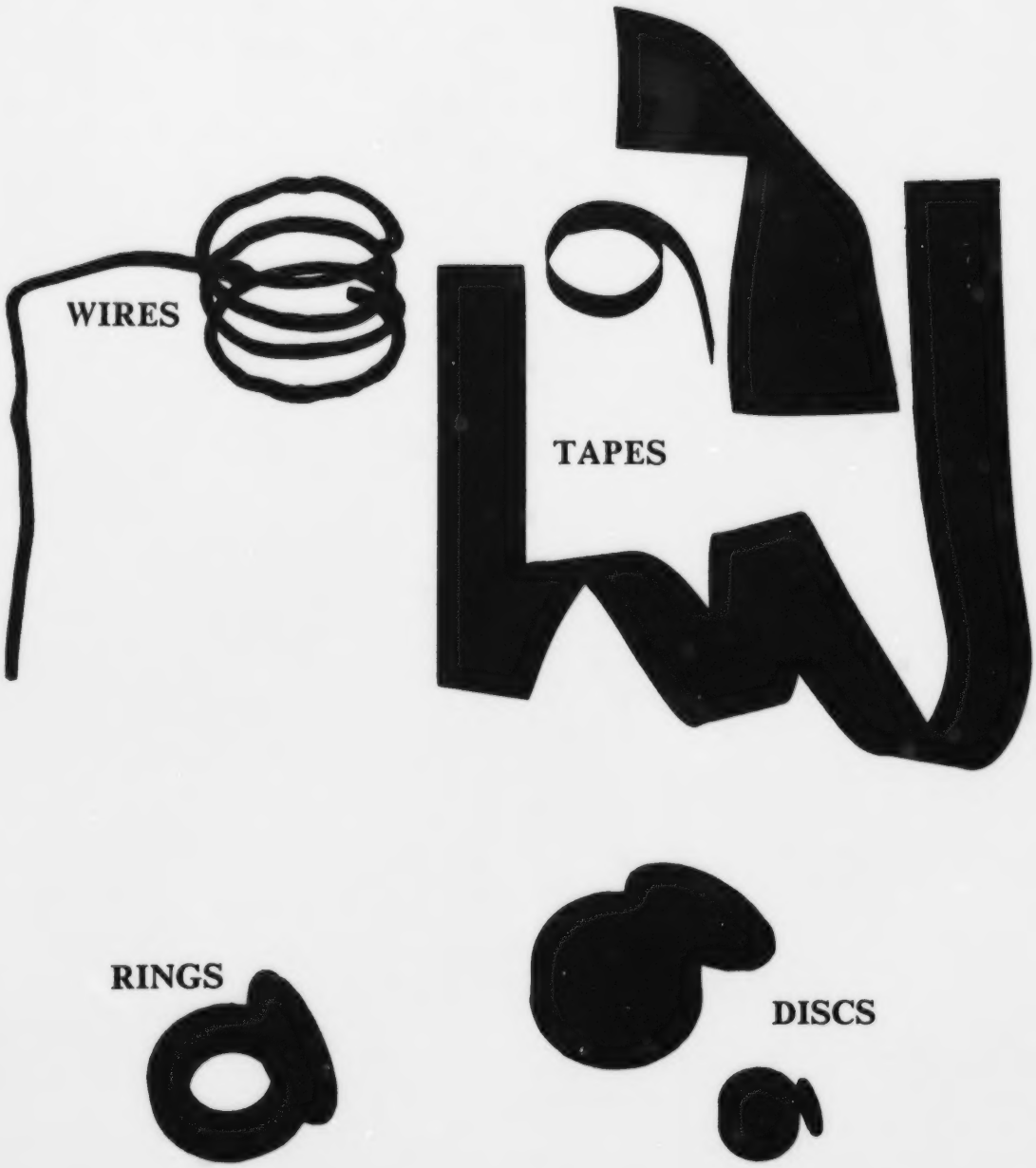

FIGURE 11

VARIOUS FORMS OF HTSC